9.0 STATISTICAL ANALYSIS OF QUALITY CONTROL DATA

To assure that the sampling and analytical protocols employed in the CAP Study were producing data of sufficient quality, a number of different quality control (QC) samples were included in the study design. The intended purpose of each QC sample varied, but each sample type belonged to one of three categories:

1. Field QC Samples, originating in the field, that assess the quality of the sample collection procedures;

2. Sample Preparation QC Samples, originating in the sample preparation laboratory, which examine the preparation of field samples for analysis, and;

3. Instrumental Analysis QC Samples, produced in the instrument analysis laboratory, that evaluate the quantitative analysis of the samples.

These individual categories reflect distinct goals of the QC analysis, and separate steps in the collection and analysis of a sample. From a statistical analysis perspective, however, the QC samples may be partitioned somewhat differently. This partitioning reflects the nature of the parameter considered when assessing a particular QC measure. Specifically, the QC samples are partitioned analytically into three groups: (1) blank samples, (2) recovery samples, and (3) duplicate samples. Table 9-1 below is helpful in considering these two approaches to categorizing the QC results. Each type of QC sample employed in the CAP Study is identified within a particular cell of the table. For example, spiked samples were analyzed as recovery samples, but their results address the quality of the sample preparation procedures. A total of ten QC measures were employed. Detailed results of the statistical analyses performed on these QC measures are reported in the sections that follow by

analysis category. Within each category, the implications of the results to each procedure step are discussed.

Table 9-1. QC Sample Categorization Matrix

	Field QC	Sample Preparation QC	Instrument Analysis QC
Blank Samples	• trip blanks • field blanks	• method blanks	• calibration blanks
Recovery Samples		• spikes • blind reference materials	• interferant check standards • calibration verifications
Duplicate Samples	• side-by-sides	• spiked duplicates	

As an overall summary, the following conclusions may be drawn regarding the QC samples:

1. Analysis of the blank samples suggests little if any procedural contamination. The majority of blanks were measured with a lead content below the instrumental level of detection.

2. Despite some procedural problems in their creation and analysis, the results for the recovery samples indicate very good method performance.

3. Spiked duplicate samples created in the laboratory exhibited very good agreement. Side-by-side field samples, on the other hand, suggest significant variability in field sampling. Greater inherent variation was seen in dust samples than in soil samples.

4. There is no significant evidence of a time-based trend in any of the QC samples.

9.1 BLANK SAMPLES

Blank samples are expected, by the nature of their collection and preparation, to contain very little or no lead. In the CAP Study, four types of blank samples were analyzed: trip blanks, field blanks, method blanks, and calibration blanks. For all but the trip blanks, the parameter of interest was the

amount of lead (µg) measured for the sample (lead content). For the trip blanks and also for the field blanks, the net weight (g) of the sample was also examined. Evidence of a significant amount of lead in a blank sample would suggest a bias in the results for the regular field samples. As was the case for the regular field data, the lead content of the blanks was assumed to follow a lognormal distribution. The amounts, therefore, were log-transformed before statistical analysis.

9.1.1 Field Quality Control

Trip blanks are vacuum dust cassettes that are weighed in the gravimetric laboratory before and after being transported to the field. They are similar to field blanks, except they are not exposed to the field environment. Trip blanks provide information on the sample weight variability resulting from gravimetric laboratory activities in the absence of field handling. Used in combination with the field blank net weight data, they provide a means of determining the error contribution from the gravimetric laboratory should the net weight data from the field blanks show an unusual result. Accordingly, no lead analysis was performed on trip blanks. One trip blank was generated for each housing unit by selecting, at random, one vacuum dust cassette from all unused cassettes transported to the field.

Descriptive statistics for the net weights measured for both trip and field blanks from the CAP Pilot and CAP Studies are presented in Table 9-2. The number of samples, arithmetic mean, standard deviation, minimum and maximum net weights are presented. Net weight data from trip blanks indicate that gravimetric laboratory processing resulted in a mean net weight gain of 3.5 mg. This gain is about twice as large as that observed during the Pilot study which had a mean net weight gain

of 1.8 mg. The weight difference between the CAP Study and CAP Pilot Study can be attributed, in part, to protocol changes made

Table 9-2. Net Weight Results for Trip and Field Blanks

Statistic	CAP Pilot Study		CAP Study	
	Trip Blanks	Field Blanks	Trip Blanks	Field Blanks
Number of Samples	54	9	51*	52
Net Weight Mean (mg)	1.8	2.4	3.5	0.4
Net Weight Standard Deviation (mg)	0.3	0.5	1.2	3.0
Minimum Net Weight (mg)	1.1	1.4	0.2	-6.3
Maximum Net Weight (mg)	2.6	3.0	5.1	5.2

* Excluding one sample identified as an outlier.

in gravimetric processing. The clearance criterion for the determination of cassette stability was increased from ± 1 mg to ± 2 mg. This change was made to reduce the excessive equilibration time required during the pilot study. It was anticipated that the resulting losses in accuracy at low sample weights would be offset by the increased collection efficiency of the sampling system used for dust sample collection. Indeed, the summary in Table 2-1 of the amount of dust collected suggests that the amount of collected dust was sufficiently large to override the weight gain bias resulting from gravimetric laboratory processing.

Field blanks are identical to regular field samples, except that no sample is actually collected. Field blanks provide information on the extent of lead contamination experienced by field samples resulting from a combination of laboratory

processing and field handling. In addition, field blanks for cassettes provide information on the sample weight variability

resulting from the combination of gravimetric laboratory activities and field handling. Field blanks for vacuum dust, wipe dust (abated houses only), and soil cores were collected for each housing unit.

Field blanks, as opposed to trip blanks, better represent the handling experienced by field samples. Any adjustments to weight data, if required, are best based on field blank net weight data. As shown in Table 2-1, the mean weights of collected dust for field samples are considerably larger than the mean net weight of 0.4 mg measured for the field blanks shown in Table 9-2. No adjustments were made, therefore, to field sample weights of vacuum dust cassettes for the calculation of lead concentration (µg/g) values or lead loading (µg/ft^2) values.

Mean net weights between the trip and field blanks for the CAP Pilot were relatively close as indicated in Table 9-2. However, mean net weights between the trip and field blanks for the CAP Study differ more considerably. The CAP Study data imply that field handling produces a weight reduction in the vacuum dust cassettes. The change between the CAP Pilot and CAP Study data is suspected to be related to a combination of two factors: the protocol changes made in gravimetric processing discussed earlier, and the lack of humidity at the sampling site.

Handling of field blanks exposes the cassettes to the atmosphere at the field site. The procedure for collecting field blanks included the following steps: remove the cassette from the sealed plastic bags, open the cassette casing, insert it into the cyclone sampler, remove it from the sampler, close the cassette casing, and replace the cassette into the sealed plastic bags used for transport. Trip blanks were not removed from their sealed plastic bags in the field. The collection site was in an area known for low humidity; Denver has a dry climate. When opened in a low humidity environment, field blanks would be expected to lose water (and weight) absorbed during equilibration

in the gravimetric laboratory. It is suspected that the change in gravimetric clearance criterion did not permit sufficient equilibration time in the gravimetric laboratory to allow the cassettes to gain back all the weight lost during their exposure to the low humidity field environment. This would account for the observed net weight difference between the field and trip blanks. Gravimetric records were reviewed for data to support this supposition. However, no weights were recorded for the first 72 hours after vacuum dust cassettes were placed into the gravimetric laboratory (standard equilibration) and there exist no field humidity data. There are insufficient data available, as a result, to either discount or support the protocol change and humidity effect explanation.

Field blank samples also were measured for lead content. A summary of the field blank lead content results (and in fact, of all the QC results) is presented in Table 9-3. The descriptive statistics reported include the number of samples, number above the instrumental detection limit (IDL), minimum and maximum. When possible, the geometric mean and logarithmic standard deviation for the amount of lead per sample are presented. A 95% upper confidence bound on the 95th percentile for lead content is also provided. For the sake of simplicity, this bound will be referred to as the estimated 95% tolerance bound. These calculations were possible only when a sufficient number of results were above the IDL.

If all results were above the IDL, calculation of the geometric mean and logarithmic standard deviation was routine, and the estimated 95% tolerance bound was determined using an exact procedure for lognormal distributions. In cases where a portion of the results were below the IDL, statistical procedures which recognize these data as censored values were used to estimate the geometric mean and logarithmic standard deviation. A lognormal model was fitted to the data and its parameters

estimated. The SAS procedure LIFEREG was utilized in obtaining these estimates. LIFEREG maximizes the log-likelihood function via a ridge stabilized Newton-Raphson algorithm, thereby

Table 9-3. Results of Quality Control Analyses

Quality Control Measure		Parameter Considered	# of Samples[1]	Minimum	Maximum	Geometric Mean	Log Standard Deviation	Lower Tolerance Bound[3]	Upper Tolerance Bound[3]
Field Blanks	Vacuum	Amount (µg)	52 (6)	0.344	2.682	0.228	1.059		2.006
	Wipe		34 (1)	2.723	35.445	na	na		na
	Soil		51 (4)	1.198	35.638	0.067	2.387		9.162
Method Blanks	Vacuum	Amount (µg)	48 (13)	0.468	20.681	0.414	1.135		4.369
	Wipe		6 (1)	2.723	3.975	na	na		na
	Soil		22 (1)	1.276	3.297	na	na		na
Calibration Blanks		Amount (µg)	431 (33)	0.0004	0.068	0.007	0.956		0.041
Blind References	I	% Recovery	38	0.851	1.231	1.016	0.088	0.841	1.227
	II		37	0.344	1.749	1.109	0.274	0.615	1.999
	III		37	0.229	1.131	0.881	0.316	0.447	1.736
ICS		% Recovery	144	0.997	1.211[2]	1.060	0.035	0.993	1.131
Calibration Verifications		% Recovery	274	0.962	1.058	1.014	0.016	0.986	1.043
Spikes	Vacuum	% Recovery	96	0.930	1.428	1.030	0.068	0.904	1.174
	Wipe		12	0.862	1.000	0.926	0.044	0.820	1.044
	Soil		44	0.733	1.309	0.981	0.098	0.799	1.205
Spiked Duplicates	Vacuum	Ratio	48	1.000	1.094	1.031	0.039		1.068
	Wipe		6	1.001	1.151	1.063	0.080		1.238
	Soil		22	1.001	1.308	1.081	0.109		1.227
Side-by-Sides	Vacuum	Ratio (loading)	52	1.027	40.381	2.334	1.110		6.403
	Vacuum	Ratio (conc.)	52	1.022	81.101	2.071	1.129		6.605
	Soil	Ratio (conc.)	51	1.004	4.569	1.296	0.399		1.951

Censored Analysis

[1] The number of samples measured above the instrumental detection limit (IDL) is enclosed in parentheses. If there is no number in parentheses, all samples were measured above the IDL.

[2] This value represents an extra ICS analyzed in the middle of an analysis run from an instrument analysis batch containing no field samples. This batch contained only re-runs of SRM No. 1646 under the conditions described in Section 9.2.1. The next highest ICS, 1.182, was also measured in the same analysis batch.

[3] The lower tolerance bound represents a lower 95 percent confidence bound on the 5th percentile; the upper tolerance bound represents on upper 95 percent confidence bound on the 95th percentile. Where both are provided, combined they represent a 90 percent tolerance interval.

na - The statistic could not be calculated due to the large number of censored samples.

providing maximum likelihood estimates of the log mean and log standard deviation. Further, an approximate procedure was used to calculate the estimated 95% tolerance bound. The "approximate" nature of this statistical procedure was in employing the "censor" estimates for log mean and log standard deviation in calculating a traditional 95% tolerance bound. Since this procedure did not include an adjustment to the bounds reflecting censored data, the estimated tolerance bound is approximate.

The data for field blank samples, and other blank samples, are illustrated in Figure 9-1. The amount of lead (µg) found in each blank sample is plotted by sample type. Different plotting symbols are used to indicate whether the result was above the IDL or below, in which case the detection limit is plotted. In those instances where an estimated tolerance could be calculated, the estimated 95% tolerance bound is illustrated in the figure by a bar which has the bound as its upper value.

Most of the field blanks generated for each sample type were below the IDL: more than 88% of the vacuum dust samples were, as well as more than 97% of the wipe dust samples, and more than 92% of the soil samples. No field blank result exceeded five times the average IDL measured during the analysis activities (0.037 µg of lead per mL). Geometric means for all three sample types are less than this IDL mean. These data suggest that no lead contamination occurred during field sample activities.

9.1.2 Sample Prep Quality Control

Method blanks are blank samples generated in the laboratory during sample preparation activities. They are processed in a manner identical to field samples except that no sample material or sample medium is present in the container used for sample digestion. Method blanks provide information on the potential lead contamination experienced by field samples resulting solely from laboratory processing. Method blanks were generated at a

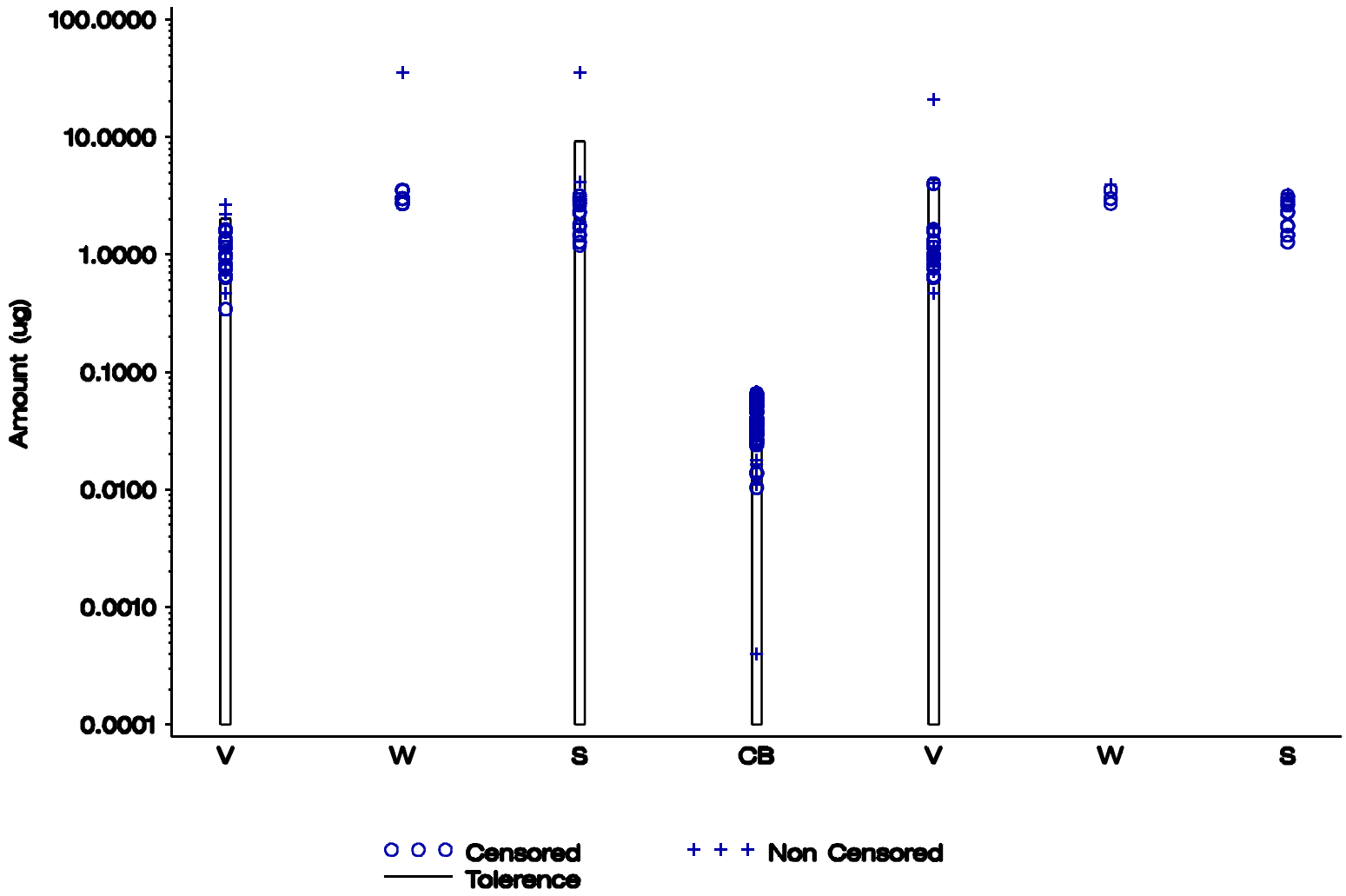

Figure 9-1. Individual measurements and tolerance bounds for µg lead/sample in blank samples.

frequency of two samples per batch of approximately 40 field samples.

A summary of the method blank results is presented in Table 9-3 and presented graphically in Figure 9-1. These results were obtained using the same procedures outlined for field blanks. All method blank data met the data quality objective of lead levels less than 10 times the IDL. Most of the method blanks generated for each sample type were below the IDL: 72% of the vacuum dust samples, 83% of the wipe dust samples, and 95% of the soil samples. In fact, a geometric mean, log standard deviation, and approximate 95% tolerance bound could only be calculated for the vacuum cassettes. Only one method blank result exceeded five times the average IDL measured during the analysis activities (0.037 µg of lead per mL). This method blank was one of two in a sample preparation batch which contained only high sample weight vacuum dust samples with a minimum field sample weight of 4 grams each. This method blank, with a measured lead level near six times the instrumental detection limit, was insignificant with respect to the lead levels within the batch. The other method blank in this high sample weight batch was less than the IDL. These data indicate no lead contamination occurred during laboratory processing of field samples.

9.1.3 Instrumental Analysis Quality Control

Calibration blanks were analyzed along with field samples to assure adequate instrument performance during lead determinations. They are useful in assessing any changes in instrument performance which may affect the estimated lead concentrations reported for regular field samples. Descriptive statistics summarizing the results for calibration blanks are presented in Table 9-3. The individual results and their approximate 95% tolerance bound are portrayed in Figure 9-1. As with the field blank results, the geometric mean, log standard

deviation, and approximate 95% tolerance bound are adjusted to reflect the censored nature of many of the results. Greater than

92% of the calibration blanks, which included both initial and continuing calibration blanks, were below the IDL. The maximum lead concentration measured for any calibration blank was less than two times the average IDL for all instrumental analysis runs (0.037 µg of lead per mL). Their geometric mean was well below the average IDL. These results suggest that the field sample results are free from any significant bias caused by carryover.

9.2 RECOVERY SAMPLES

Recovery samples are prepared to contain a known total amount of lead or to have had a known amount of lead added (spiked). Four types of recovery samples were incorporated into the design of the CAP Study: blind reference material samples, spiked samples, calibration verification samples, and interferant check standards (ICS). The parameter of interest was the ratio of the amount of lead measured for the sample (lead content) to the known amount of lead in the sample. This ratio should be approximately one, and when multiplied by 100 is commonly referred to as the percent recovery. Percent recovery values over 100% indicate a measured value exceeding the known amount of lead in the sample and values under 100% indicate a measured value below the known amount. Spiked soil samples were slightly different in that the spike was added to a sample already containing a measureable amount of lead. The percent recovery value is assumed to follow a lognormal distribution. If the geometric mean of the lognormal distribution is 100%, this is an indication that lead is over-recovered half the time and under-recovered half the time.

Normally, there is a difference between blind reference material samples and spiked samples. Blind reference samples are created by adding a known amount of lead to a blank sample, while spiked samples are created by adding a known amount of lead to a split field sample. These procedures were utilized with the soil

samples. In the case of dust samples, blank cassettes and clean wipes were used for the blind reference material samples and for the spiked samples, and there were no split dust samples involved in the creation of the spiked dust samples. Split dust samples were not attempted because of the difficulty in dividing dust samples in a homogenous manner. Hence, the samples labelled as dust spiked samples were made the same way as the samples labelled as dust blind reference material samples. Spiked samples and blind reference samples were inserted into the batch processing stream to monitor the performance of the chemical analysis.

9.2.1 Sample Preparation Quality Control

Spiked samples were blank samples or regular field soil samples fortified with known levels of lead prior to sample preparation activities, and processed in a manner identical to field samples. They provided lead recovery information for assessing the accuracy and precision of field sample data through sample preparation and analysis activities. Spiked samples were generated at a frequency of four (two spikes and two spiked duplicates) per batch of approximately 40 field samples.

As is noted earlier, spiked soil samples were prepared and analyzed somewhat differently from vacuum and wipe dust spikes. Whereas spiked cassette and wipe samples involved spiking a known amount of lead into a blank, spiked soil samples were created by spiking a regular soil sample with a known amount of lead. For cassette and wipe spikes, the ratio of measured amount to known spiking amount was considered (percent recovery). However, since a soil spike sample already contained some lead, a different calculation of percent recovery was required. Specifically, the spiked soil percent recovery was determined as,

$$\frac{\left[\begin{matrix}measured\ \mu g\ lead\\ for\ spiked\ sample\end{matrix}\right] - \left[\begin{matrix}measured\ \mu g\ lead\\ for\ unspiked\ sample\end{matrix}\right]}{\mu g\ lead\ for\ spike} * 100.$$

Use of spike data to assess the accuracy and precision achieved for field samples is partially dependent on the matrix

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matching between the QC sample and field sample. This is because data generated from a given analytical processing scheme are generally matrix sensitive. In the case of soil samples, the matrix matching was very good, because unspiked and spiked samples were generated from splits of homogenized soil samples. Spiked sample data for soils, therefore, were expected to closely mimic that of the field samples. However, as noted earlier, blank cassettes and wipes were used for the unspiked and spiked samples for dust. As a result, the spiked sample QC data for dust samples may be less useful than the spiked sample QC data generated for soils. Still, the spiked sample QC data do provide an adequate measure of the degree of successful execution of the analytical methodology. The sample preparation and analysis methodology is procedurally very similar to methods commonly used and verified successfully for many different types of environmental samples. The spiked sample QC data for dust samples generated during this project are still useful in estimating of precision and accuracy for field samples.

A summary of the spiked sample results is presented in Table 9-3. Descriptive statistics presented include the number of samples, minimum, maximum, geometric mean, and log standard deviation. In addition, an estimated central 90% tolerance interval was calculated using an exact procedure for lognormal data. This interval was derived from a 95% upper confidence bound on the 95th percentile and a 95% lower confidence bound on the 5th percentile. Performance-Control charts showing individual spiked sample recovery data are shown for each sample type in Figures D-1, D-2, and D-3 of Appendix D.

The data for all recovery samples, including the spiked samples, are illustrated in Figure 9-2. The individual percent recovery results for each type of recovery sample are plotted. The estimated central 90% tolerance interval is presented in the figure by a bar extending from the lower confidence bound on the

5th percentile to the upper confidence bound on the 95th percentile.

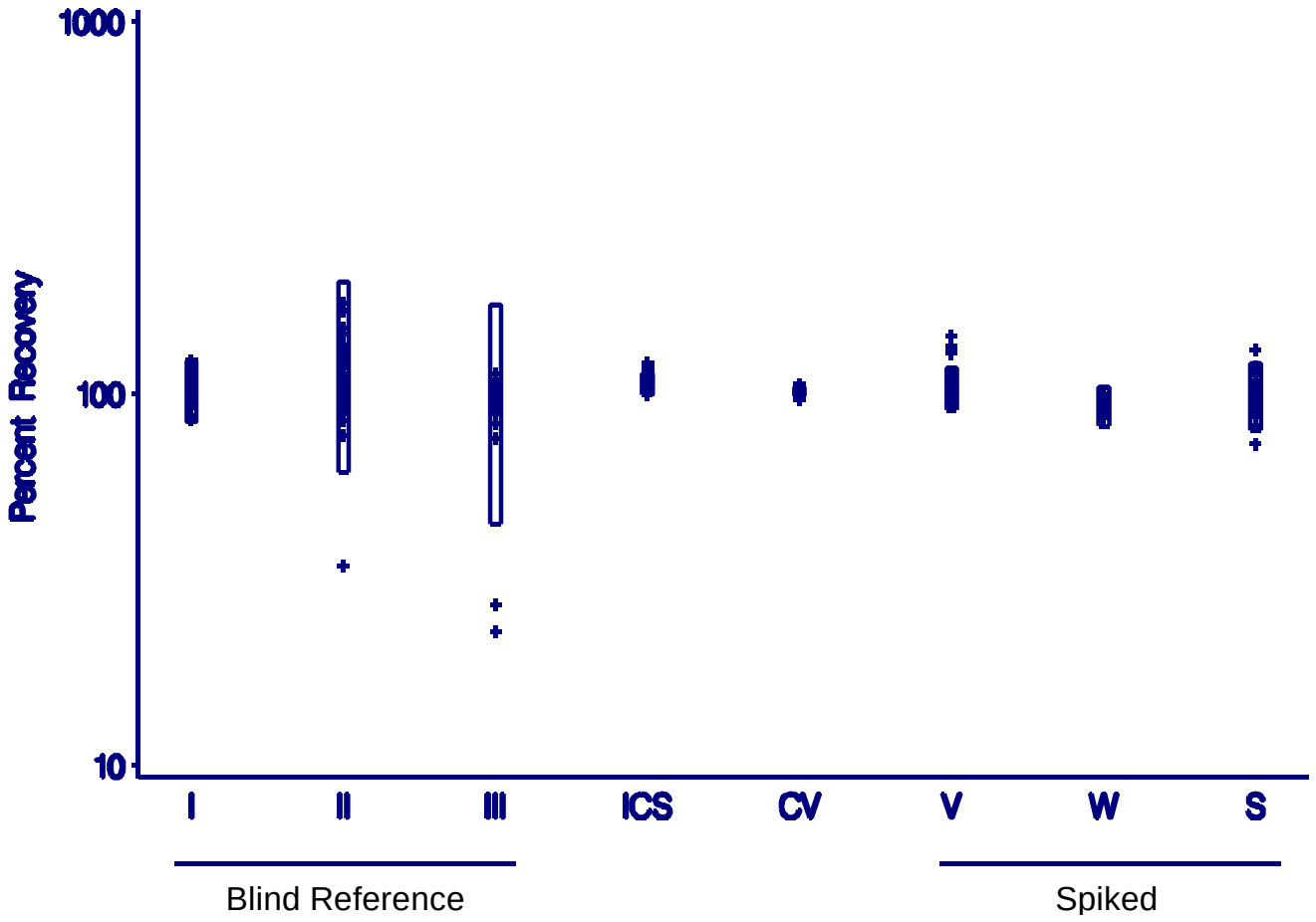

Figure 9-2. Individual measurements and tolerance bounds for percent recovery in recovery samples.

Spiked sample recoveries for all but four data points met the data quality objectives of accuracy of ±20% from the true spiked value. Three of these four points were the result of a spiking error. Specifically, the samples were spiked 10 times less than planned. This error produced measurements approaching both the IDL and background lead levels detected in blankcassettes used in the generation of the spiked samples. Accurate determination of spike recoveries under such conditions is difficult and is not anticipated to be reflective of performance related to field samples. The other data point (soil sample) was only slightly outside the data quality objective (130.9%). Geometric means for all three sample types are within ±10% of the true spiked amount. The estimated tolerance intervals for all three media contain 100% or complete recovery. These data imply that accuracy for field samples was good and well within data quality objectives.

Blind reference material samples were generated by placing known quantities of NIST standard reference materials (SRMs) into blank samples and inserting them into the sample batches in a blind manner prior to sample preparation activities. These reference materials were processed by the laboratory in the same way as the field samples. Their results provide lead recovery information that can be used as an assessment of accuracy of field sample data as determined by sample preparation and analysis activities. The blind nature of the insertion into the sample processing stream helped provide QC data unbiased by laboratory activities. Blind reference materials were generated at a frequency of two (one each of two different materials) per batch of approximately 40 field samples.

As was discussed for the spiked QC samples earlier, matrix matching is an important determinant of the usefulness of QC samples in assessing the accuracy achieved for regular field samples. In general, reference materials are included in an

analysis scheme to help provide higher confidence in the accuracy of field sample data than can be obtained using only spiked

samples. Unfortunately when this study was initiated, no suitable dust or soil SRMs were available. Two SRMs were chosen as the best available approximations to the anticipated matrices of the field samples. The matching was achieved with respect to general matrix components and anticipated lead levels. These were NIST SRM No. 2704 Buffalo River Sediment and NIST SRM No. 1646 Estuarine Sediment. Given the limitations of the matrix match, some caution is appropriate in extending the accuracy results of these reference materials. These data, combined with the spiked results, still do provide reasonable confidence that analytical methodologies were carried out as planned.

Performance-Control charts, showing the percent recovery of lead from the two blind reference materials, are shown for each sample type in Figures D-4, D-5, and D-6. Blind reference material recoveries for NIST SRM No. 2704 met the data quality objectives for accuracy of ±30% from the true spiked value. Recoveries for NIST SRM No. 1646, however, were sporadic. Eight of 37 data points were outside data quality objectives. Investigation into these recovery problems suggested they were related to corrections for spectral interferences during instrumental analysis measurements. SRM No. 1646 has a low lead concentration (28.2 µg/g) combined with high levels of other metals such as iron. The iron-to-lead ratio is over 1000 to 1. In order to correct for potential iron interferences, the analyst conducting the instrumental measurements must perform serial dilution of all digests to get iron levels within the calibration range of the ICP instrument. For field samples, extra dilutions were rarely needed, which indicates limits to the ability of SRM No. 1646 to mimic field sample matrices. For the blind SRM No. 1646 reference materials, extra dilution was always required. This extra dilution pushed the measurable lead level down to within a few multiples of the instrumental detection limit where measurement variance increases relative to digests with higher

concentrations of lead. The result of these extra dilutions were the sporadically poor recoveries seen for SRM No. 1646.

The sporadic recoveries for SRM No. 1646 were verified by reanalyzing the original digests using the ICP-AES reconfigured to extend the linear range of the instrument for detecting iron. In this way the extra dilution requirement was avoided. The results of the measurements are plotted as the DF=1 data points in the Performance-Control charts shown. Using the reconfigured instrument, all but two blind reference material recoveries for NIST SRM No. 1646 met the data quality objectives of accuracy of ±30% from the true spiked value. The remaining two points were associated with extra high weight sample batches that required a sample preparation protocol change. The change resulted in a four-fold increase in final digestion volume. The increase, in turn, reduced lead levels to values close to the IDL.

Blind reference material results, shown in Table 9-3, are partitioned into three groups depending upon the standard reference material used. Results for SRM No. 2704 are identified as Group I, while the original analysis results for SRM No. 1646 are identified as Group II. The results of the reanalysis of SRM No. 1646 (data points plotted in the figures as DF=1) are identified as group III. These results are illustrated in Figure 9-2. The geometric means were within ±12% of the NIST certified value. The estimated central 90% tolerance intervals all contain 100% recovery. Even with the matrix match limitations for these SRMs, these data imply that accuracy for field samples was good and well within data quality objectives.

9.2.2 Instrumental Analysis Quality Control

Calibration verification samples were analyzed along with field samples during instrumental measurement activities to verify calibration standard levels and monitor drift of instrument response. A summary of lead results for calibration verification samples is shown in Table 9-3 and Figure 9-2. These

statistics are calculated using the same procedures described for spiked samples. All calibration verification results met design specifications. In addition, the estimated central 90% tolerance interval is narrow and contains 100%. It seems reasonable to conclude that the field sample results are free from any significant bias caused by instrumental drift.

Interference check standards (ICS) were used to verify accurate analyte response in the presence of possible spectral interferences from other analytes present in the sample. A summary of lead results for ICS is available in Table 9-3 and Figure 9-2. As with the calibration verifications, the estimated central 90% tolerance interval is remarkably narrow and contains 100%. There is no evidence of any significant bias in the regular field sample results caused by commonly encountered interferences.

9.3 DUPLICATE SAMPLES

Duplicate samples are expected to be have similar lead content either because they were collected side-by-side in the field or because they were created to be comparable in the laboratory. In both cases, such samples were analyzed one after the other in the same analytical batch. The analytical result of interest for each pair of duplicate samples was the ratio of the larger measured lead result to the smaller measured lead result. This ratio has a minimum value of one. The log of this ratio was assumed to follow the absolute value of a normal distribution with mean zero and standard deviation F. In the CAP Study, two types of duplicate samples were examined: side-by-side samples collected in the field, and spiked duplicate samples created in the sample preparation laboratory.

9.3.1 Field Quality Control

Side-by-sides were included to determine variability due to the sample collection process; however, this source of variability will also be confounded with short-scale variations attributable to nearby sampling locations within a room or local sampling area. Side-by-sides were collected for dust vacuum and soil core samples. A pair of dust and soil duplicates were collected at each housing unit surveyed.

Table 9-3 reports descriptive statistics for the side-by-side samples. The statistics presented are the number of samples collected, minimum ratio, maximum ratio, geometric mean ratio, and log standard deviation. An estimated 95% tolerance bound was also calculated, using an exact procedure for the distribution assumed for the log transformed ratio.

The side-by-side results are illustrated in Figure 9-3. The ratio for each pair of samples is plotted by sample type. The estimated 95% tolerance bound is portrayed in the figure by a bar extending from a value of one up to the tolerance bound.

The soil side-by-sides exhibit better agreement than the vacuum dust pairs. Their geometric mean was approximately 40% smaller than that for the paired dust vacuum lead concentrations. The inherent variability between field samples, however, is evident in these results. Despite being collected side-by-side, a number of the pairs were measured to have very different lead contents. This disparity is reflected in the higher ratios and relatively large estimated tolerance bounds.

9.3.2 Sample Preparation Quality Control

Spiked duplicate samples originate in the sample preparation laboratory and are developed with identical lead content. Each pair is derived from two identical spiked samples. The spiked sample results are presented in Section 9.2.1 where a more detailed presentation of their development is available. Spiked duplicates were generated at a frequency of two pair (two spikes

and two spiked duplicates) per batch of approximately 40 field samples.

A summary of the spiked duplicate sample results is presented in Table 9-3. This summary is portrayed graphically in Figure 9-3. The descriptive statistics are the same as those developed for the field side-by-side samples. Performance-4

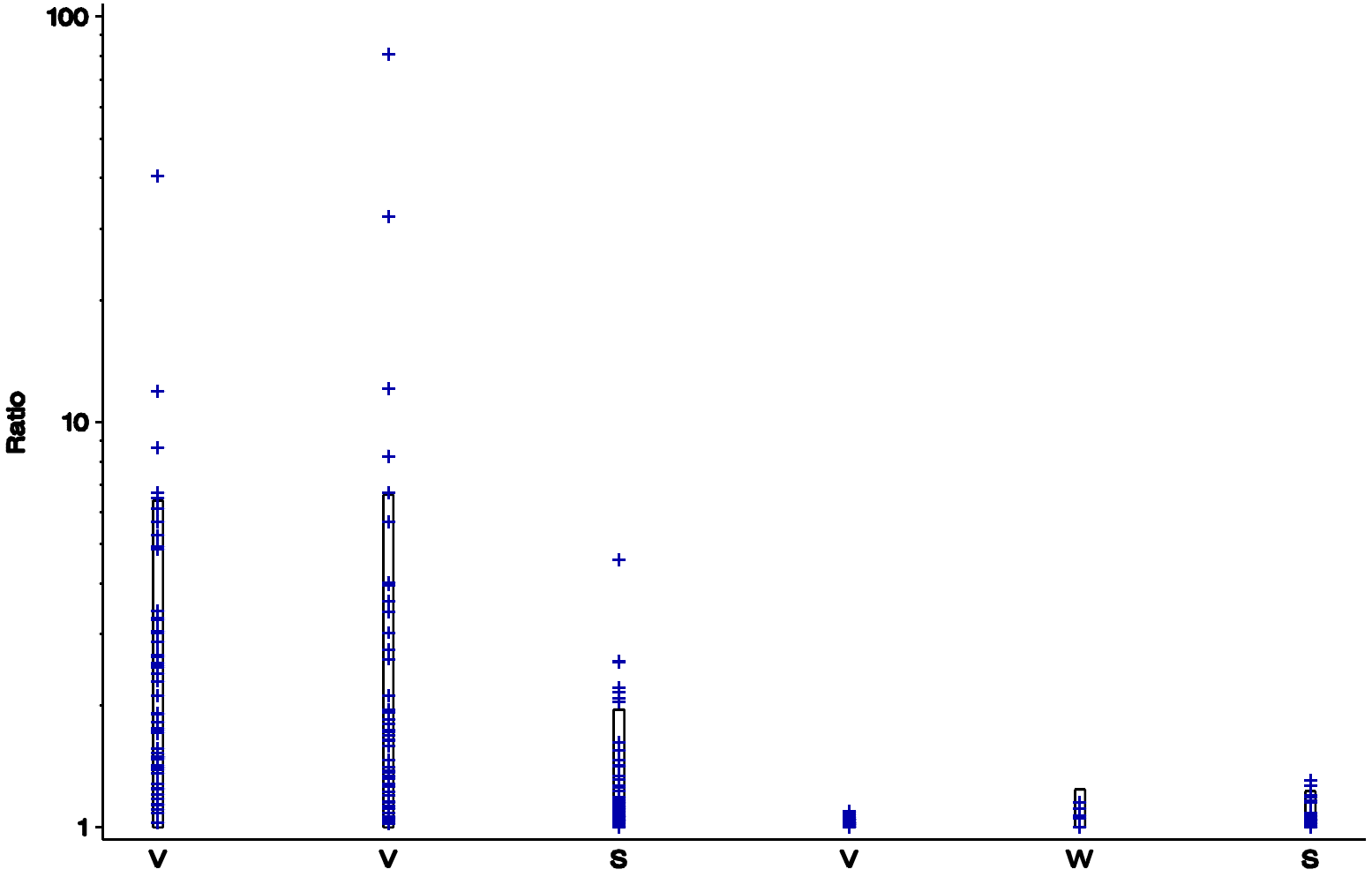

Figure 9-3. Individual measurements and tolerance bounds for the ratio of duplicate samples.

Control charts showing the range of spiked sample and spiked sample duplicate pairs are shown for each sample type in Figures D-7, D-8, and D-9.

The range of spiked duplicate percent recoveries were tighter for dust samples than for soil samples. This is not surprising given the sampling protocol. Recall that spiked blanks were employed for dusts, since cassettes and wipes could not be split homogeneously, and regular field sample splits were utilized for soils (see Section 9.2.1). The ranges observed for soils imply that the 0.5 gram nominal sample weight used for sample preparation may not be sufficient to overcome some heterogeneity apparently still present in the dried, sieved, and homogenized soil samples used for analysis. Figure D-9 shows that the range for four of the spiked duplicate soil sample pairs was above the control limit. Still, the geometric means are close to one and the estimated 95% tolerance bounds are not unreasonably large. The results do suggest good agreement between the spiked duplicate samples.

9.4 TIME TREND ANALYSES

The extensive samples collected in the CAP Study required laboratory analyses which spanned several months. One natural question, therefore, was whether any trend across time was apparent in the samples. Specifically, is there a time-based bias in the sampling results? The QC samples, expected to demonstrate consistent sampling results, are ideal for this examination.

The individual results for each of the QC measures outlined above were plotted using a common frame of reference. Each QC sample was plotted according to the instrument analysis batch it was included in, and its run number within that batch. The instrument batches were ordered based on the time they were processed. For each QC sample type, the appropriate parameter was displayed for the individual results. The measured amount of

lead (µg), for example, was displayed for the 52 vacuum dust field blank results.

An examination of these plots suggested no evidence of time trends, except for the soil field blank and method blank results. Recall that more than 92% of the soil field blank results were censored, as were 95% of the soil method blanks. In the results, censored samples are set equal to the instrumental detection limit. Furthermore, these blanks were all analyzed using the same dilution factor (50 mL). Their apparent time trends were determined, therefore, to be a function of the IDLs for the instrument batches containing the soil samples. Figure 9-4 presents the available IDL results for each instrument batch. Those batches which included soil samples are identified as circles. Note that they do exhibit an apparent quadratic trend across time. The IDLs considered as a whole, in contrast, show no evidence of a trend. To assess the significance of the apparent trend in the soil IDLs, quadratic equations were fit to all the IDLs and only to those including soil samples. The two resulting fits were not significantly different (p=0.13). Given the apparent randomness exhibited by the IDLs, there is no evidence of a time trend in the soil field or method blank results.

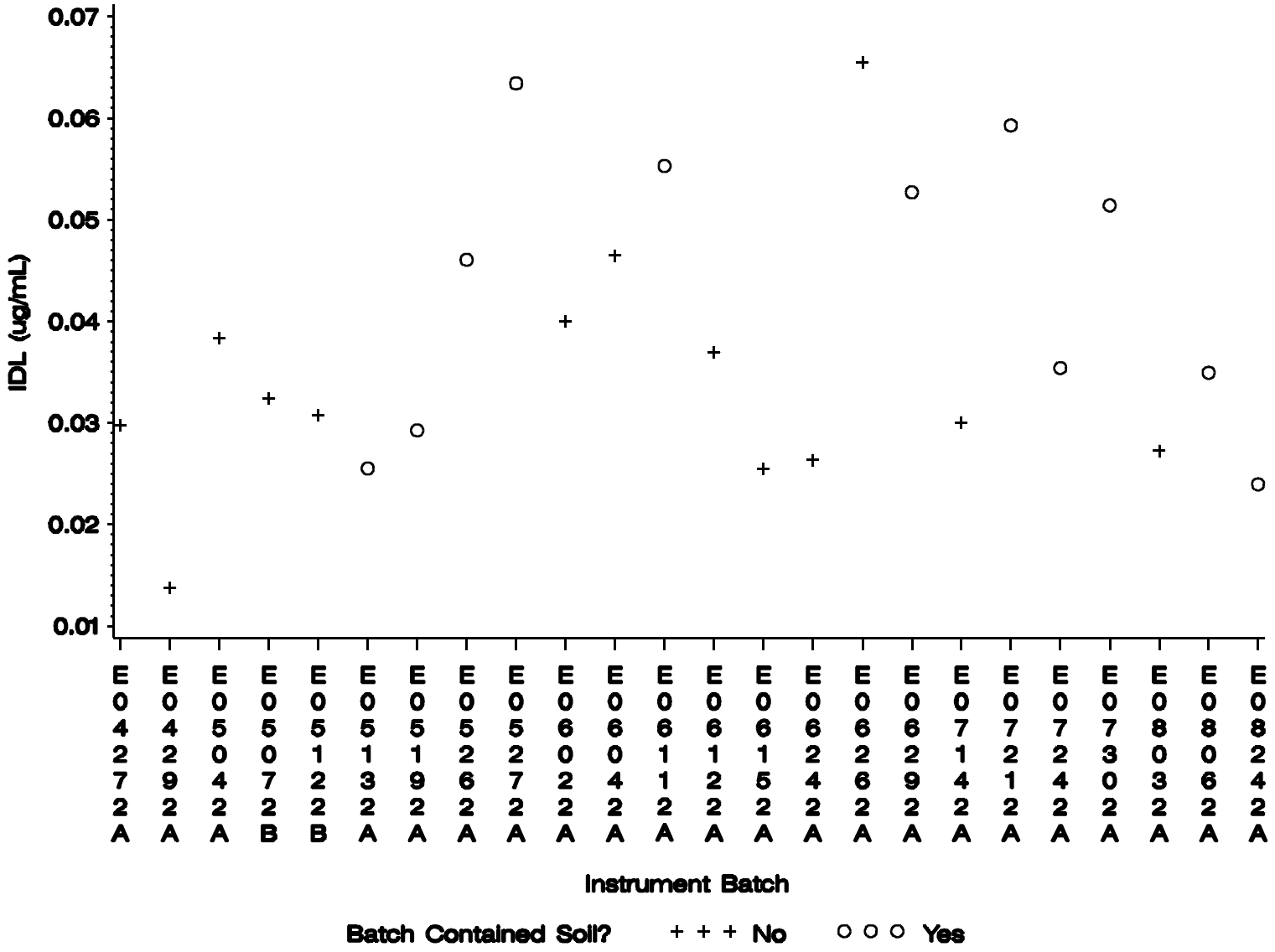

Figure 9-4. Time trend analyses in instrumental detection level by instrument batch.